Claims

1. A proton-conducting polymer membrane which is based on polyazoles and is obtainable by a process comprising the steps
   A) mixing of one or more aromatic tetraamino compounds with one or more aromatic carboxylic acids or esters thereof which contain at least two acid groups per carboxylic acid monomer, or mixing of one or more aromatic and/or heteroaromatic diaminocarboxylic acids, in phosphoric acid to form a solution and/or dispersion,
   B) heating of the solution and/or dispersion obtained in step A) to temperatures of up to 350°C, preferably up to 280°C, to form the polyazole polymer,
   C) application of a layer using the mixture from step B) to a support,
   D) treatment of the membrane formed in step C).

2. The membrane as claimed in claim 1, characterized in that 3,3',4,4'-tetraaminobiphenyl, 2,3,5,6-tetraaminopyridine, 1,2,4,5-tetraaminobenzene, bis(3,4-diaminophenyl)sulfone, bis(3,4-diaminophenyl) ether, 3,3',4,4'-tetraaminobenzophenone, 3,3',4,4'-tetraaminodiphenylmethane and 3,3',4,4'-tetraaminodiphenyldimethylmethane are used as aromatic tetraamino compounds.

3. The membrane as claimed in claim 1, characterized in that isophthalic acid, terephthalic acid, phthalic acid, 5-hydroxyisophthalic acid, 4-hydroxyisophthalic acid, 2-hydroxyterephthalic acid, 5-aminoisophthalic acid, 5-N,N-dimethylaminoisophthalic acid, 5-N,N-diethylaminoisophthalic acid, 2,5-dihydroxyterephthalic acid, 2,5-dihydroxyisophthalic acid, 2,3-dihydroxyisophthalic acid, 2,3-dihydroxyphthalic acid, 2,4-dihydroxyphthalic acid, 3,4-dihydroxyphthalic acid, 3-fluorophthalic acid, 5-fluoroisophthalic acid, 2-fluoroterephthalic acid, tetrafluorophthalic acid, tetrafluoroisophthalic acid, tetrafluoroterephthalic acid, 1,4-naphthalenedicarboxylic acid, 1,5-naphthalenedicarboxylic acid, 2,6-naphthalenedicarboxylic acid, 2,7-naphthalenedicarboxylic acid, diphenic acid, 1,8-dihydroxynaphthalene-3,6-dicarboxylic acid, bis(4-carboxyphenyl) ether, benzophenone-4,4'-dicarboxylic acid, bis(4-dicarboxyphenyl) sulfone, biphenyl-4,4'-dicarboxylic acid, 4-trifluoromethylphthalic acid, 2,2-bis(4-carboxyphenyl)hexafluoropropane, 4,4'-stilbenedicarboxylic acid, 4-carboxycinnamic acid, or their C1-C20-alkyl esters or C5-C12-aryl esters, or their acid anhydrides or acid chlorides are used as aromatic dicarboxylic acids.

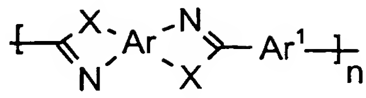
4. The membrane as claimed in claim 1, characterized in that tricarboxylic acids, tetracarboxylic acids or their C1-C20-alkyl esters or C5-C12-aryl esters or their acid anhydrides or their acid chlorides, preferably 1,3,5-benzenetricarboxylic acid (trimesic acid); 1,2,4-benzenetricarboxylic acid (trimellitic acid); (2-carboxyphenyl)iminodiacetic acid, 3,5,3'-biphenyltricarboxylic acid; 3,5,4'-biphenyltricarboxylic acid and/or 2,4,6-pyridinetricarboxylic acid, are used as aromatic carboxylic acids.

5. The membrane as claimed in claim 1, characterized in that tetracarboxylic acids, their C1-C20-alkyl esters or C5-C12-aryl esters or their acid anhydrides or their acid chlorides, preferably benzene-1,2,4,5-tetracarboxylic acid; naphthalene-1,4,5,8-tetracarboxylic acid, 3,5,3',5'-biphenyltetracarboxylic acid; benzophenonetetracarboxylic acid, 3,3',4,4'-biphenyltetracarboxylic acid, 2,2',3,3'-biphenyltetracarboxylic acid, 1,2,5,6-naphthalenetetracarboxylic acid, 1,4,5,8-naphthalenetetracarboxylic acid, are used as aromatic carboxylic acids.

6. The membrane as claimed in claim 4, characterized in that the content of tricarboxylic acids and tetracarboxylic acids (based on dicarboxylic acid used) is from 0.5 to 20 mol%.

7. The membrane as claimed in claim 1, characterized in that heteroaromatic dicarboxylic acids and tricarboxylic acids and tetracarboxylic acids containing at least one nitrogen, oxygen, sulfur or phosphorus atom in the aromatic, preferably pyridine-2,5-dicarboxylic acid, pyridine-3,5-dicarboxylic acid, pyridine-2,6-dicarboxylic acid, pyridine-2,4-dicarboxylic acid, 4-phenyl-2,5-pyridinedicarboxylic acid, 3,5-pyrazoledicarboxylic acid, 2,6–pyrimidine-dicarboxylic acid, 2,5-pyrazinedicarboxylic acid, 2,4,6-pyridinetricarboxylic acid, benzimidazole-5,6-dicarboxylic acid, and their C1-C20-alkyl esters or C5-C12-aryl esters, or their acid anhydrides or their acid chlorides are used as heteroaromatic carboxylic acids.

8. The membrane as claimed in claim 1, characterized in that a polyazole-based polymer comprising recurring azole units of the general formula (I) and/or (II) and/or (III) and/or (IV) and/or (V) and/or (VI) and/or (VII) and/or (VIII) and/or (IX) and/or (X) and/or (XI) and/or (XII) and/or (XIII) and/or (XIV) and/or (XV) and/or (XVI) and/or (XVII) and/or (XVIII) and/or (XIX) and/or (XX) and/or (XXI) and/or (XXII)



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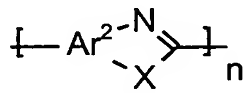

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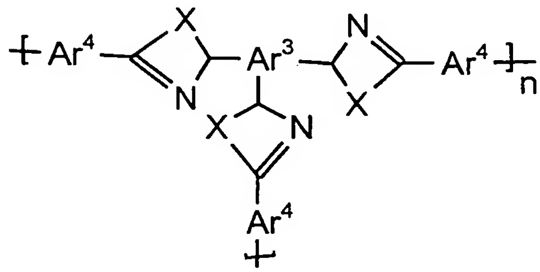

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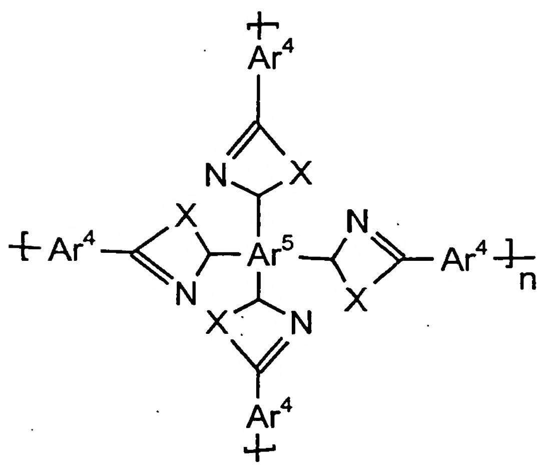

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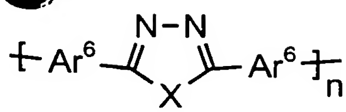

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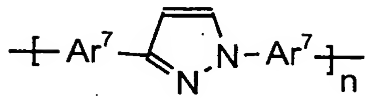

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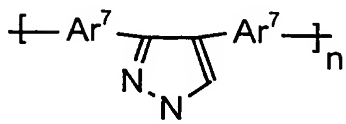

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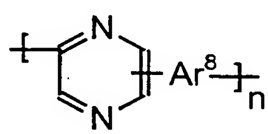

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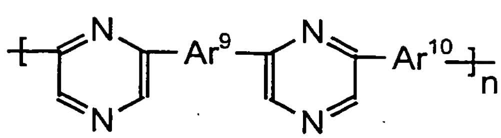

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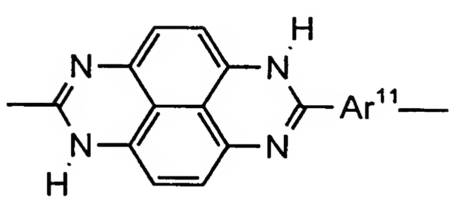

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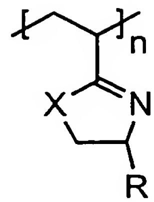

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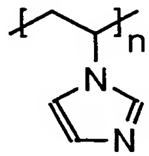

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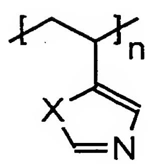

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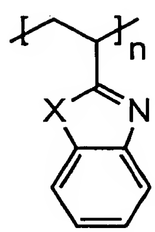

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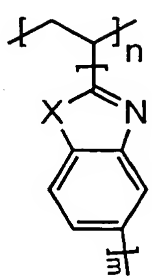

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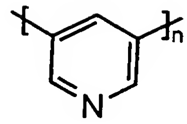

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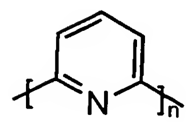

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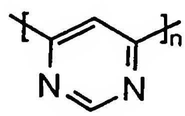

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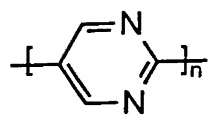

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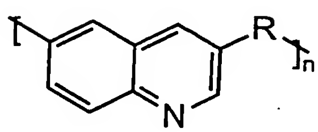

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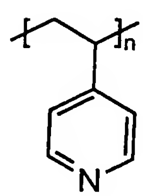
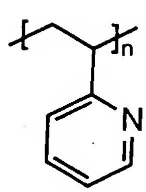


(XXI)



(XXII)

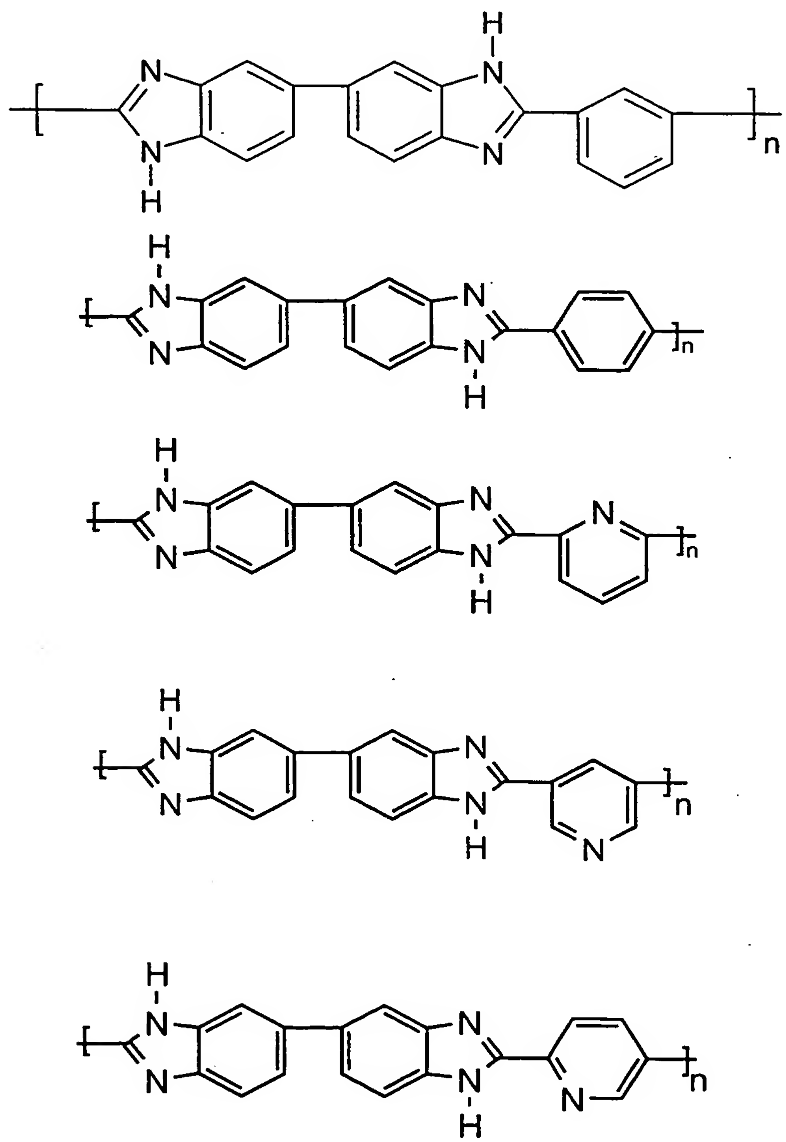
where

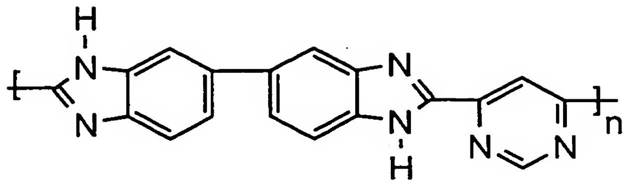
the radicals Ar	are identical or different and are each a tetravalent aromatic or heteroaromatic group which can be monocyclic or polycyclic,
the radicals Ar^1	are identical or different and are each a divalent aromatic or heteroaromatic group which can be monocyclic or polycyclic,
the radicals Ar^2	are identical or different and are each a divalent or trivalent aromatic or heteroaromatic group which can be monocyclic or polycyclic,
the radicals Ar^3	are identical or different and are each a trivalent aromatic or heteroaromatic group which can be monocyclic or polycyclic,
the radicals Ar^4	are identical or different and are each a trivalent aromatic or heteroaromatic group which can be monocyclic or polycyclic,
the radicals Ar^5	are identical or different and are each a tetravalent aromatic or heteroaromatic group which can be monocyclic or polycyclic,
the radicals Ar^6	are identical or different and are each a divalent aromatic or heteroaromatic group which can be monocyclic or polycyclic,
the radicals Ar^7	are identical or different and are each a divalent aromatic or heteroaromatic group which can be monocyclic or polycyclic,
the radicals Ar^8	are identical or different and are each a trivalent aromatic or heteroaromatic group which can be monocyclic or polycyclic,
the radicals Ar^9	are identical or different and are each a divalent or trivalent or tetravalent aromatic or heteroaromatic group which can be monocyclic or polycyclic,
the radicals Ar^{10}	are identical or different and are each a divalent or trivalent aromatic or heteroaromatic group which can be monocyclic or polycyclic,
the radicals Ar^{11}	are identical or different and are each a divalent aromatic or heteroaromatic group which can be monocyclic or polycyclic,
the radicals X	are identical or different and are each oxygen, sulfur or an amino group which bears a hydrogen atom, a group having 1-20 carbon atoms, preferably a branched or unbranched alkyl or alkoxy group, or an aryl group as further radical,
the radicals R	are identical or different and are each hydrogen, an alkyl group or an aromatic group and
n, m	are each an integer greater than or equal to 10, preferably greater than or equal to 100,

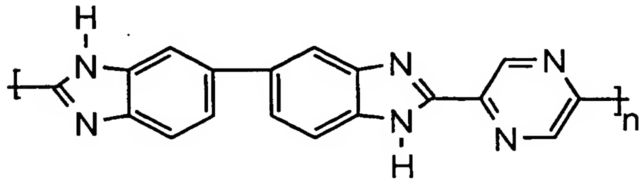
is formed in step B).

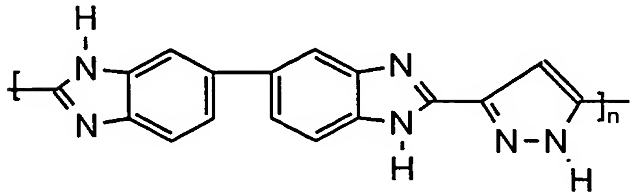
9. The membrane as claimed in claim 1, characterized in that a polymer selected from the group consisting of polybenzimidazole, poly(pyridines), poly(pyrimidines), polyimidazoles, polybenzothiazoles, polybenzoxazoles, polyoxadiazoles, polyquinoxalines, polythiadiazoles and poly(tetrazapyrenes) is formed in step B).

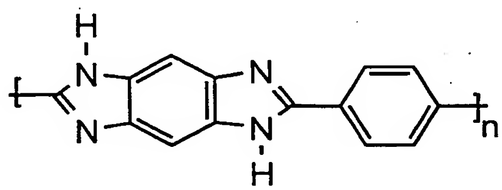
10. The membrane as claimed in claim 1, characterized in that a polymer comprising recurring benzimidazole units of the formula

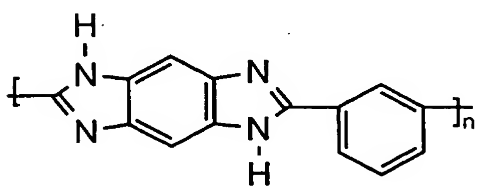


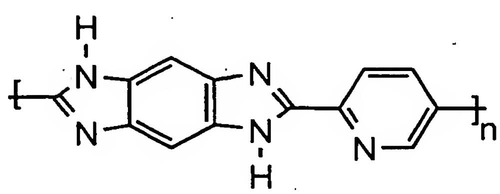


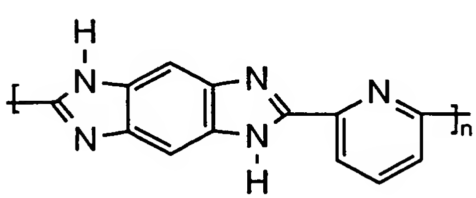


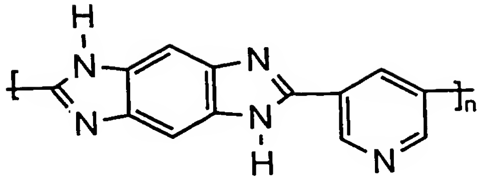


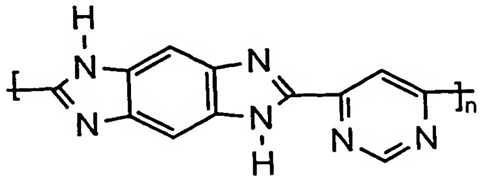


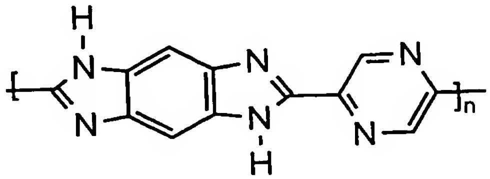


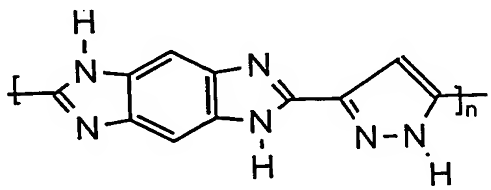


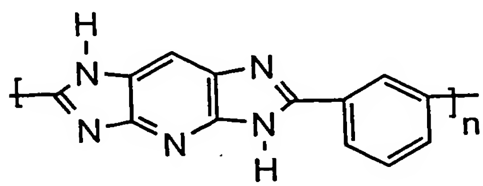


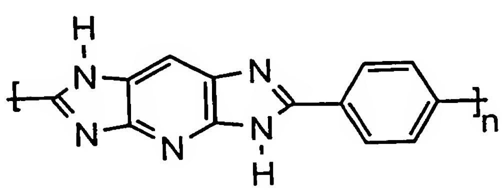


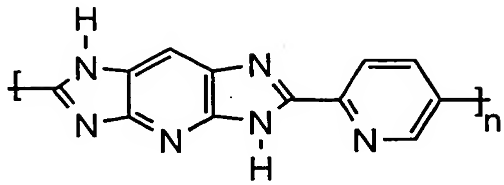


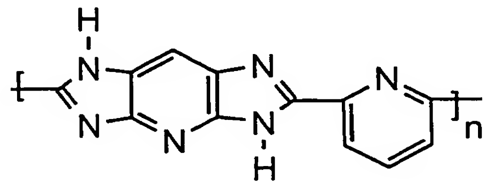


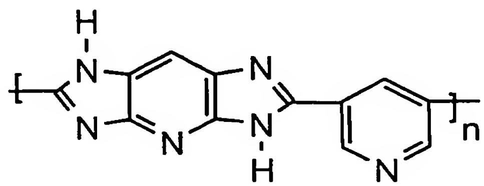


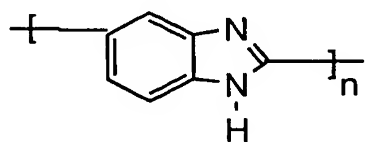


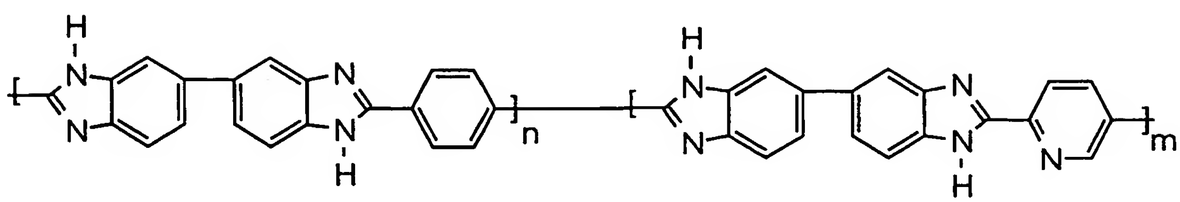


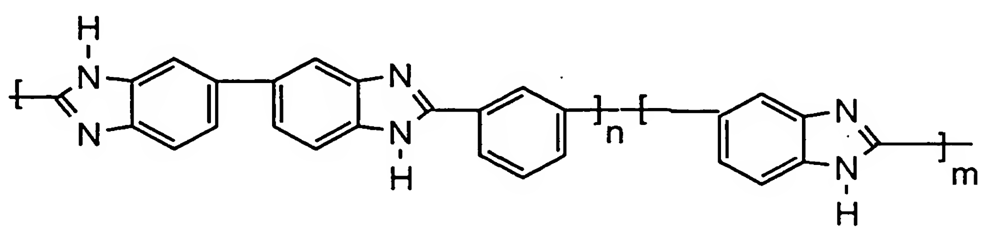












where n and m are each an integer greater than or equal to 10, preferably greater than or equal to 100,
is formed in step B).

11. The membrane as claimed in claim 1, characterized in that the viscosity is adjusted by addition of phosphoric acid after step B) and before step C).

12. The membrane as claimed in claim 1, characterized in that a layer having a thickness of from 20 to 4000 μm, preferably from 30 to 3500 μm, in particular from 50 to 3000 μm, is produced in step C).

13. The membrane as claimed in claim 1, characterized in that the membrane produced in step C) is treated in step D) until the membrane is self-supporting and can be detached from the support without damage.

14. The membrane as claimed in claim 1, characterized in that the membrane produced in step C) is treated in step D) by the action of heat in the presence of atmospheric oxygen.

15. The membrane as claimed in claim 1, characterized in that the membrane produced in step C) still contains tricarboxylic or tetracarboxylic acids which are crosslinked in step D).

16. The membrane as claimed in claim 1, characterized in that the membrane produced in step C) is crosslinked by treatment with sulfuric acid in step D).

17. The membrane as claimed in claim 1, characterized in that the membrane produced in step C) is crosslinked by action of IR or NIR light or by irradiation with ß-rays in step D).

18. The membrane as claimed in claim 1, characterized in that it has a layer comprising a catalytically active component.

19. The membrane as claimed in claim 1, characterized in that the formation of the membrane according to steps A) to D) is carried out on a support or a support film on which the catalyst is present, and the catalyst is located on the membrane according to the invention after removal of the support or the support film.

20. The membrane as claimed in claim 1, characterized in that the formation of the membrane according to steps A) to D) is carried out on an electrode as support.

21. An electrode provided with a proton-conducting polymer coating which is based on polyazoles and is obtainable by a process comprising the steps
    A) mixing of one or more aromatic tetraamino compounds with one or more aromatic carboxylic acids or esters thereof which contain at least two acid groups per carboxylic acid monomer, or mixing of one or more aromatic and/or heteroaromatic diaminocarboxylic acids, in phosphoric acid to form a solution and/or dispersion,
    B) heating of the solution and/or dispersion obtained in step A) to temperatures of up to 350°C, preferably up to 280°C, to form the polyazole polymer,
    C) application of a layer using the mixture from step B) to an electrode,
    D) if appropriate, treatment of the membrane formed in step C).

22. The electrode as claimed in claim 21, wherein the coating has a thickness in the range from 2 to 3000 μm, preferably from 3 to 2000 μm, in particular from 5 to 1500 μm.

23. A membrane-electrode unit comprising at least one electrode and at least one membrane as claimed in one or more of claims 1 to 20.

24. A membrane-electrode unit comprising at least one electrode as claimed in claim 21 or 22 and at least one membrane as claimed in one or more of claims 1 to 20.

25. A fuel cell comprising one or more membrane-electrode units as claimed in claim 22 or 23.

26. A polymer film which is based on polyazoles and is obtainable by a process comprising the steps
    A) mixing of one or more aromatic tetraamino compounds with one or more aromatic carboxylic acids or esters thereof which contain at least two acid groups per carboxylic acid monomer, or mixing of one or more aromatic and/or heteroaromatic diaminocarboxylic acids, in phosphoric acid to form a solution and/or dispersion,
    B) heating of the solution and/or dispersion obtained in step A) to temperatures of up to 350°C, preferably up to 280°C, to form the polyazole polymer,
    C) application of a layer using the mixture from step B) to a support,
    D) treatment of the membrane formed in step C) until it is self-supporting,

E) detachment of the membrane formed in step C) from the support,

F) removal of the phosphoric acid present and drying.

27. The polymer film as claimed in claim 25, characterized in that the removal of the phosphoric acid in step F) is carried out by means of a treatment liquid.

28. The use of the polymer film as claimed in claim 25 or 26 for the filtration and/or separation of gases and/or liquids or in reverse osmosis.

29. A polymer which is based on polyazoles defined in claims 8 to 10, whose molecular weight expressed as intrinsic viscosity is at least 1.4 dl/g and which is obtainable by a process comprising the steps

A) mixing of one or more aromatic tetraamino compounds with one or more aromatic carboxylic acids or esters thereof which contain at least two acid groups per carboxylic acid monomer, or mixing of one or more aromatic and/or heteroaromatic diaminocarboxylic acids, in phosphoric acid to form a solution and/or dispersion,

B) heating of the mixture obtainable according to step A) under inert gas to temperatures of up to 350°C, preferably up to 280°C, to form the polyazole polymer,

C) precipitation of the polymer formed in step B) and isolation and drying of the polymer powder obtained.

30. A molding comprising polymers as claimed in claim 18.

31. A polymer fiber which is based on polyazoles, whose molecular weight expressed as intrinsic viscosity is at least 1.4 dl/g and which is obtainable by a process comprising the steps

A) mixing of one or more aromatic tetraamino compounds with one or more aromatic carboxylic acids or esters thereof which contain at least two acid groups per carboxylic acid monomer, or mixing of one or more aromatic and/or heteroaromatic diaminocarboxylic acids, in polyphosphoric acid to form a solution and/or dispersion,

B) heating of the mixture obtained in step A) to temperatures of up to 350°C, preferably up to 280°C, to form the polyazole polymer,

C) extrusion of the polyazole polymer formed in step B) to form fibers,

D) introduction of the fibers formed in step C) into a liquid bath,

E) isolation and drying of the fibers obtained.

32. The polymer fiber as claimed in claim 30, characterized in that the fibers formed in step C) are introduced into a precipitation bath.